

A New Method for the Determination of Adsorption and Activation Volumes by Pressure Modulation

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One of the fundamental issues in interfacial electrochemistry is the actual charge of adsorbed species. The measurable quantity „electrosorption valency“ is not suited to give an information on the actual (partial) charge.

In homogeneous chemical kinetics, a knowledge of the charge of the activated complex allows a distinction between inner-sphere and outer sphere reactions. It can be very well estimated from the activation volume, which is largely determined by electrostriction and which is given by the pressure dependence of the reaction rate.^{1,2} Similarly, it should be possible to deduce the charge of adsorbed species from their volumes of adsorption. However, the high pressures of up to 50 kbar usually required make an application to interfacial studies difficult.

We therefore developed a new instrument (fig. 1), in which the pressure is modulated with an amplitude of only ± 0.5 bar with the help of piezo transducer. The small effect on the reaction rate, potential or charge of the electrode can be detected using the lock in technique. The determination of the reaction volume of the redox couple $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ served to control the reliability of the instrumentation. The pressure dependence of the equilibrium potential is given by the reaction volume ΔV^R :

$$-nF \frac{\partial E}{\partial p} = \Delta V^R$$

Under pressure modulation, with $\delta p = p_0 \sin \omega t$, this leads to an oscillation of the equilibrium potential according to $\delta E = (\partial E / \partial p) \delta p = (\Delta V / nF) \cdot p_0 \sin \omega t$. The reaction volume thus determined is $(-32 \pm 4) \text{ cm}^3 \text{ mol}^{-1}$ and therefore very close to literature values^{3,4}.

Similarly, for an adsorption reaction, the pressure dependence of the equilibrium constant is given by

$$d \ln K = -\frac{\Delta V^{\text{ad}}}{RT} dp$$

and thus, with $I = nF d\Gamma/dt$, the adsorption volume is given by

$$\Delta V^{\text{ad}} = -\frac{I_A RT}{p_A \omega n F \Gamma},$$

where I_A is the amplitude of the resultant current amplitude and where a simple Henry isotherm was assumed. In practice, the pressure dependence of the reference electrode and the phase shift (important for higher electrolyte resistances) have to be taken into account as well.

As a first model system we studied the adsorption of hydrogen at polycrystalline Pt. We found a value of $4.8 \text{ cm}^3 \text{ mol}^{-1}$. Together with the partial molar volume for protons in water ($-5.4 \text{ cm}^3 \text{ mol}^{-1}$) measured by

Zana⁵ the partial molar volume of the adsorbed hydrogen is nearly zero.

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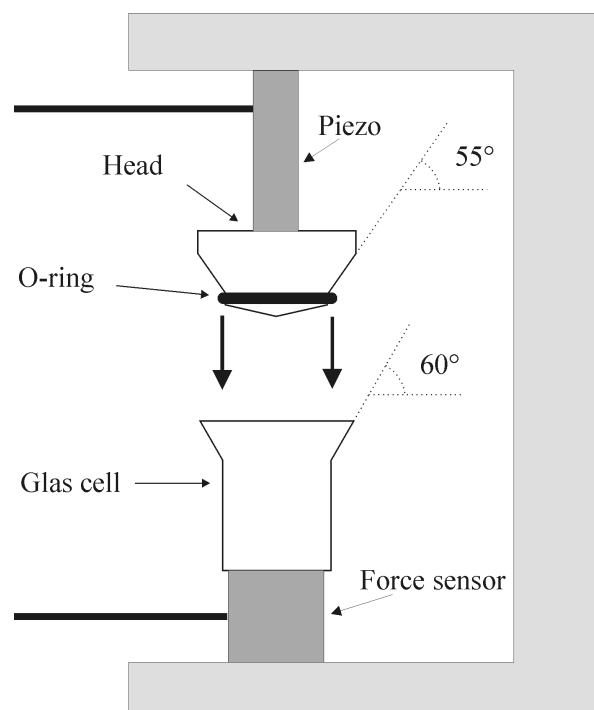


Figure 1: setup of the pressure cell